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S. V. LEBEDEV'S WORK ON THE SYNTHESIS OF RUBBER

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The greatest advance by the chemical industry in the 20th century -- the synthesis of rubber -- is inseparably connected with the name of the most outstanding organic chemist in the USSR, Academician Sergey Vasil'yevich Lebedev. Chemical science found in him a worthy follower of A. M. Butlerov in the field of the chemistry of unsaturated hydrocarbons.

Lebedev established principles for the polymerization of these compounds and for their synthesis. He also applied his results in this field to the solution of problems connected with the synthesis of rubber on an industrial scale.

Sergey Vasil'yevich Lebedev was born 25 July 1874. Upon leaving Petersburg University in 1900, he began work in the chemical industry, and in 1906 took up systematic scientific research work. He chose to study the field of polymerization of unsaturated hydrocarbons, beginning with the esters of acrylic acids.

Shortly thereafter, he began the study of the polymerization of diethylene hydrocarbons, a field practically unknown at the time he entered it. As a result of his work from 1908 to 1912, he was able to demonstrate for the first time the ability of several butadiene derivatives to polymerize into rubberlike products (1909). This is significant in view of the fact that every country in the world now uses butadiene as the basic monomer in its synthetic rubber industry.

Lebedev established (1) the nature of the basic products formed in the process of thermal polymerization of diethylene hydrocarbons, and (2) the relationship between the rate of the thermal polymerization of these compounds and their structure (the effect of substituents).

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He also established recognized laws in this field which formed the basis of further studies. It is 40 years since he formulated his principles, and nothing fundamentally new in this field has been discovered since then by either USSR or foreign scientists. Synthetic rubber was prepared for the first time in the Soviet Union in 1926-1932 in accordance with his methods.

According to Lebedev, temperature plays a very important role in the formation of polymers and dimers. The relative amounts of the polymers and the dimers depend on the temperature. With an increase in temperature, the amount of the dimer increases, and that of the polymer decreases.

This rule has a very important practical value. The dimers of butadiene derivatives are derivatives of cyclohexene and are formed, as he pointed out, invariably along with the polymers. In order to obtain a maximum yield of the polymers, the process must be carried out at relatively low temperatures. Lebedev's experiments with isobutylene demonstrated that the products at high temperatures were low molecular, and at low temperatures were high molecular.

In the second principle governing the polymerization of butadiene derivatives, he established the relation between the rate of polymerization and the structure of the hydrocarbons, stating the following three conditions:

1. In a series of isomers, as the substituents are moved from the end atoms of a conjugate system to the middle atoms, the rate of polymerization increases; if the substituents are moved in a reverse direction, it decreases.

2. The formation of a ring by a chain having a conjugate system increases the rate of polymerization.

3. In a homologous series, an increase in the mass of the substituents at the middle atoms of a conjugate system increases the rate of polymerization, but an increase at the end atoms decreases the rate of polymerization, if heating is carried out at the same temperatures.

Application of this rule to the synthesis of rubber permits the selection of the most suitable hydrocarbons for the process.

Lebedev advanced a new concept relating polarity to polymerization in his M. A. thesis, "Research in the field of Polymerization of Diethylene Hydrocarbons," published in 1913. In this thesis, Lebedev stated that as a result of studying the mechanism of the process, he assumed that the molecule reacts at only one point in forming a compound and that the formation of the compound is determined by two factors: the affinity of the unsaturated atoms and the polarity. This monograph, still used and still unsurpassed, also dealt with allene hydrocarbons.

The Russian Academy of Sciences awarded Lebedev the Prize imeni Tolstoy in 1914. His works, however, were not fully appreciated in Czarist Russia, and only after the Great October Revolution and the coming-to-power of the Bolshevik Party did they receive the merited attention.

Following the announcement (by the Supreme Soviet for the National Economy) of competition for the development of an industrial method for the synthesis of rubber, he and his scientists set out in 1926 to develop such a method, and on 1 January 1928, he won the prize by presenting the jury with a 2-kilogram specimen of synthetic rubber (butadiene, as indicated previously, being the basis for the process).

Lebedev began by working on the preparation of butadiene from both petroleum and ethyl alcohol, but soon found that the latter method was preferable. According to his method, alcohol is simultaneously dehydrated and dehydrogenated to give a high yield of butadiene according to the equation: $2C_2H_5OH \longrightarrow C_4H_6 + 2H_2O + H_2$.

Through his efforts, and now with the sponsorship and aid of the government of the USSR, Stalin and his closest aides, Kirov and Ordzhonikidze, the first synthetic rubber factory was built in 1932, and others followed. During the building of the factories and afterward his functions were chiefly supervisory and technological.

Lebedev was awarded the Order of Lenin by the Central Executive Committee of the USSR in 1931, and in 1932 he became an Active Member of the Academy of Sciences USSR.

From 1920 to 1934, he conducted a whole series of experiments on the hydrogenation and polymerization of unsaturated compounds, establishing the connection between their structures and the rates of their hydrogenation, another study which is closely allied with the field of synthetic rubber. For this, in 1930, he was awarded the Prize imeni F. E. Dzerzhinskiy.

His work on the polymerization of ethylene hydrocarbons by silicates is the scientific basis for the preparation of liquid fuel from gaseous hydrocarbons. It also forms the foundation for the synthesis of rubber by the polymerization of isobutylene, a process which was first studied by Lebedev and led to later industrial application of the reaction in question. Through the years, his efforts are characterized by unity of purpose and persistence.

In the academic realm, Lebedev was a professor at Leningrad University and also at the Military Medical Academy imeni Kirov. In later years he was, in addition, a professor at the Leningrad Technological Institute. He taught many organic chemists, who, since his death in 1934, are carrying on his work.

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